

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

a. REPORT SECURITY CLASSIFICATION
Unclassified

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

3. DISTRIBUTION/AVAILABILITY OF REPORT

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

Available for public release.
Distribution unlimited.

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

5. MONITORING ORGANIZATION REPORT NUMBER(S)

#55

6a. NAME OF PERFORMING ORGANIZATION

6b. OFFICE SYMBOL
(If applicable)

7a. NAME OF MONITORING ORGANIZATION

The Pennsylvania State Univ.

Office of Naval Research

6c. ADDRESS (City, State, and ZIP Code)

7b. ADDRESS (City, State, and ZIP Code)

Department of Chemistry
The Pennsylvania State University
University Park, Pa 16802Arlington
Virginia 122178a. NAME OF FUNDING/SPONSORING
ORGANIZATION8b. OFFICE SYMBOL
(If applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

ONR

8c. ADDRESS (City, State, and ZIP Code)

10. SOURCE OF FUNDING NUMBERS

Arlington
Virginia 22217PROGRAM
ELEMENT NO.
N00014-84PROJECT
NO.
K-0447TASK
NO. NR
356/4-6-84WORK UNIT
ACCESSION NO.

11. TITLE (Include Security Classification)

Second Order Non-Linear Optical Polyphosphazenes (Proceedings of the Symposium on
Non-Linear Optics, ACS Meeting, Boston, 1990).12. PERSONAL AUTHOR(S) A. A. Dembek, H. R. Allcock, C. Kim, W. H. Steier, R. L. S. Devine,
Yongqiang Shi, and C. W. Spangler13a. TYPE OF REPORT
Reprint

13b. TIME COVERED

FROM TO

14. DATE OF REPORT (Year, Month, Day)

1990, March 23

15. PAGE COUNT

16

16. SUPPLEMENTARY NOTATION

Chapter in ACS. Symposium Series volume (1990)

17. COSATI CODES

FIELD

GROUP

SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

Phosphazenes, polymers, synthesis, NLO materials,
optical materials

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

In this contribution we describe the synthesis and second-order optical properties of a series of mixed-substituent poly(organophosphazenes) that possess covalently attached donor-acceptor substituted, conjugated moieties. The general structure of the polymers is $[NP(OCH_2CF_3)_x(OR)_y]_n$, where $OR = -O(CH_2CH_2O)_kC_6H_4-CH=CH-C_6H_4NO_2$, where $k = 1-3$, and $-OCH_2CH_2N(CH_2CH_3)C_6H_4-N=N-C_6H_4NO_2$, and $x + y = 100\%$. The nonlinear optical properties of thin films of the polymers were investigated by using second harmonic generation, giving second-harmonic coefficients, d_{33} , in the range 4.1-34 pm/V.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT

☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL
Dr. Kenneth J. Wynne22b. TELEPHONE (Include Area Code)
202-696-441022c. OFFICE SYMBOL
NC

Office of Naval Research

Contract N00014-84-K-0477
R&T Project Code 4132007---004

Technical Report #55

SECOND ORDER NON-LINEAR OPTICAL POLYPHOSPHAZENES

(Proc. of Symp. on Non-Linear Optics, ACS Meeting, Boston, 1990)

by

Alexa A. Dembek, Harry R. Allcock^{*}, Chulhee Kim (PSU)

William H. Steier^{*}, Robert L. S. Devine, and Yongqiang Shi (USC)

Charles W. Spangler (N. Illinois U.)

Chapter in ACS Symp. Ser (1990), (G. Stucky, S. Marder, J. Sohn, eds.)

March 23, 1990

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

Reproduction in whole or in part for any purpose of the United States Government is permitted.

This document has been approved for public release and sale; its distribution unlimited.

80 08 128 005

Second-Order Nonlinear Optical Polyphosphazenes

Alexa A. Dembek¹, Harry R. Allcock¹, Chulhee Kim¹, William H. Steier²,
Robert L. S. Devine², Yongqiang Shi², and Charles W. Spangler³

¹Department of Chemistry, The Pennsylvania State University,
University Park, PA 16802. ²Department of Electrical Engineering,
University of Southern California, Los Angeles, CA 90089. ³Department
of Chemistry, Northern Illinois University, DeKalb, IL 60115.

In this contribution we describe the synthesis and second-order nonlinear optical properties of a series of mixed-substituent poly(organophosphazenes) that possess covalently attached donor-acceptor substituted, conjugated moieties. The general structure of the polymers is $[\text{NP}(\text{OCH}_2\text{CF}_3)_x(\text{OR})_y]_n$, where $\text{OR} = -\text{O}(\text{CH}_2\text{CH}_2\text{O})_k\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{C}_6\text{H}_4\text{NO}_2$, where $k = 1-3$, and $-\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_3)\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4\text{NO}_2$, and $x + y = 100\%$. The nonlinear optical properties of thin films of the polymers were investigated by using second harmonic generation, giving second-harmonic coefficients, d_{33} , in the range 4.1-34 pm/V.

| | |
|--------------------|-------------------------------------|
| Accession For | |
| NTIS CRA&I | <input checked="" type="checkbox"/> |
| DTIC TAB | <input type="checkbox"/> |
| Unannounced | <input type="checkbox"/> |
| Justification | |
| By | |
| Distribution / | |
| Availability Codes | |
| Dist | Availability Codes |
| A-1 | |



The development of polymeric nonlinear optical (NLO) materials is currently an area of intense investigation (1-4). Polymeric systems which show second harmonic generation (SHG) have conjugated aromatic molecules with electron-donor and acceptor moieties in a noncentrosymmetric array. These

nonlinear optical molecules can be "doped" into a glassy polymer matrix (5-7) or can be covalently attached to a polymer backbone (8-14). The noncentrosymmetric alignment of the nonlinear optical molecules in both approaches is achieved by heating the polymer to its glass transition temperature, at which point the chains have reorientational mobility, followed by application of a strong electric field. In this paper, we will discuss the synthesis and nonlinear optical properties of phosphazene macromolecules that possess covalently attached donor-acceptor substituted, conjugated moieties (15). The structures of the nonlinear optical side groups are illustrated in Figure 1. Polyphosphazenes offer a potential advantage in that the macroscopic properties of the polymer can be tailored by the incorporation of specific substituent groups (16-21).

Figure 1 near here.

Synthesis of Nonlinear Optical Side Groups

Our initial work involved the synthesis of side chains which have the molecular characteristics required for a nonlinear optical response. Compounds 1-3 were prepared by the use of Horner-Emmons-Wadsworth Wittig methodology (22). Compound 4 was commercially available (Aldrich) as the dye, Disperse Red 1. As outlined in Scheme I, in the first step in the synthesis of 1-3, 4-hydroxybenzaldehyde was allowed to react with chloroethanol derivatives in basic ethanol containing potassium iodide for 15 h at reflux. The benzaldehyde product was then allowed to react with diethyl(4-nitrobenzyl)phosphonate in the presence of potassium

tert-butoxide in ethylene glycol dimethyl ether for 15 h at room temperature and 1 h at 85°C to yield the stilbene side groups. Compounds 1-3 were purified by column chromatography and were recrystallized from n-hexane/methylene chloride to yield yellow solids.

Scheme I near here.

Compounds 1-4 were characterized by conventional spectroscopic techniques. For the stilbene compounds 1-3, the trans conformation of the double bond was confirmed by ^1H NMR analysis. For example, in the ^1H NMR spectrum of 1, the olefinic protons were detected as a doublet of doublets resonance at 7.23 and 7.01 ppm, with a trans coupling constant of 16.3 Hz. In addition, the ^{13}C NMR spectra of the stilbene compounds indicated the presence of a single isomer that was consistent with the desired structures. The UV/visible spectra in tetrahydrofuran solution showed a λ_{max} value for 1-3 at 378 nm (ϵ 2.6×10^4) and for 4 at 490 nm (ϵ 3.1×10^4).

Synthesis of Nonlinear Optical Phosphazene Macromolecules

The overall synthetic pathway to mixed-substituent polyphosphazenes 5-9 is described in Scheme II, and the corresponding polymer structures and composition ratios are listed in Table I. Poly(dichlorophosphazene) was prepared by the thermal ring-opening polymerization of the cyclic trimer $(\text{NPCl}_2)_3$, as described in earlier papers (16-18). The substitution reactions of poly(dichlorophosphazene) were carried out in three steps. The synthesis and purification of polymer 6 will be discussed as a representative example. In the first step, sodium trifluoroethoxide was added to

poly(dichlorophosphazene) to replace approximately 50% of the chlorine atoms. In the second step, a stoichiometric deficiency of the sodium salt of 1 was allowed to react with the partially substituted polymer. In the final step, an excess of sodium trifluoroethoxide was added to replace the remaining chlorine atoms in order to obtain a fully derivatized, hydrolytically stable polymer. This three step synthetic procedure was necessary because the direct addition of the sodium salt of 1 to poly(dichlorophosphazene) resulted in the formation of an insoluble, incompletely substituted polymeric precipitate. Polymer 6 was isolated by precipitation from the concentrated THF reaction mixture into water and was purified by dialysis against methanol/water (1:1 v/v) for 7 to 10 days.

Scheme II and Table I near here.

The preparation of soluble, single-substituent polyphosphazenes that contained species 1-4 as side groups could not be accomplished because, as noted previously, the direct addition of the sodium salt of the chromophore to poly(dichlorophosphazene) resulted in the formation of a polymeric, incompletely substituted precipitate. The precipitate was insoluble in refluxing THF as well as warm dioxane, N,N-dimethylformamide, dimethylsulfoxide, nitrobenzene and N-methylpyrrolidinone. This insolubility was attributed to both the extended rigid structure and the intrinsically high polarity of the donor-acceptor substituted, conjugated side chains. Both factors may induce extensive side group stacking and thus lead to the formation of insoluble polymers.

The preparation of soluble polymers containing species 1-4 was accomplished by the use of the polar trifluoroethoxy group as co-substituent.

The partially substituted trifluoroethoxy polymer, prepared in the first step of the polymer synthesis (see Scheme II), provided a polar environment for the incorporation of the chromophoric side chains. However, the maximum loading of the polymers by the chromophores 1-4 was limited by the solubility of the polymeric products. Hence, the side group ratios for polymers 6-9 represent a maximum incorporation range of the chromophore side group by the use of this synthetic scheme.

The preparation of mixed-substituent polymers that contained co-substituents other than trifluoroethoxy groups was also explored. This part of the investigation was carried out in an attempt to tailor the macromolecular properties, for example, glass transition temperature, solubility behavior, morphology, and film-forming ability, in order to optimize the nonlinear optical behavior. However, the aryloxy substituents, including phenoxy, 4-methylphenoxy, and 3-ethylphenoxy, as well as the alkoxy substituent, methoxyethoxyethoxy, all yielded insoluble polymers, even with low incorporation ratios (10-15%) of the chromophore. These results suggest that the highly polar trifluoroethoxy group is a necessary co-substituent for the preparation of soluble polymers containing 1-4 as side chains.

Structural Characterization and Properties of Polyphosphazenes

Characterization of polymers 5-9 was achieved by ^1H and ^{31}P NMR spectroscopy, gel permeation chromatography, differential scanning calorimetry, UV/visible and infrared spectroscopy, and elemental microanalysis. All the polymers were soluble in common organic media, such as tetrahydrofuran, acetone, and methylethyl ketone.

A typical ^{31}P NMR spectrum consisted of a sharp, singlet resonance at -8 ppm, presumably a consequence of the similar environment at the trifluoroethoxy and ethoxy-ether substituted phosphorus atoms in the mixed substituent system. In addition, the singlet resonance indicated a high degree of chlorine replacement. This was supported by the elemental microanalysis data.

The substituent ratios of the polymers were determined by ^1H NMR analysis by a comparison of the integration of the combined aromatic and vinyl resonances, which were generally between 8.4 and 6.8 ppm, with the trifluoroethoxy resonance at 4.5 ppm.

The molecular weights of polymers 5-9 were estimated by gel permeation chromatography to be in the range $M_n = 9.4 \times 10^4$ to 3.2×10^5 , $M_w > 9.3 \times 10^5$, with M_w/M_n values in the region 4-7. UV/visible spectra in tetrahydrofuran showed the same trends as the corresponding side group compounds 1-4, with λ_{max} values in the range 369-378 nm for 5-7 and 468 nm for 8. Infrared spectroscopy of thin films cast on KBr for all of the polymers showed an intense P=N stretching vibration at $1250\text{-}1200\text{ cm}^{-1}$. In addition, the absorbance for the NO_2 unit at ca. 1345 cm^{-1} was detected.

The glass transition temperature (T_g) of the mixed-substituent polyphosphazenes 5-9 varied with the loading of the chromophoric side chain and with the length of the connecting ethyleneoxy spacer group. Species with one ethyleneoxy unit comprising the spacer group generated the highest glass transition temperature. The T_g values were 19°C for 5, 25°C for 6, 25°C for 7, 54°C for 8, and 44°C for 9. No evidence of $T(1)$ or T_m transitions were detected for any of these polymer samples. Hence, the addition of the chromophoric substituent disrupts the microcrystallinity of the

single substituent polymer $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$, which has a T_g at -66°C , a $T(1)$ between 60 and 90°C , and a T_m at 240°C (24).

The colors of the polyphosphazenes corresponded to those of the chromophores employed. Thus, polymers 5-8, which contained chromophores 1-3, were yellow, while polymer 9, which contained chromophore 4, was red.

Evaluation of the Second Order Nonlinear Optical Behavior

Films of polyphosphazenes 5-9 were spin cast onto indium-tin oxide coated glass from a concentrated solution in methylethyl ketone. The solution was first filtered to remove particulate impurities and the films were heated to 80 - 85°C to remove the solvent. The thicknesses and refractive indices of the polymers were obtained from ellipsometric measurements on calibration layers, which were spun on BK7 glass substrates. Measurements on each sample were performed at four different wavelengths (634.8 nm, 753.0 nm, 802.0 nm and 852 nm) in order to minimize the errors in the extrapolated values at 532 and 1064 nm. The thickness of the layers examined ranged from 70 - 250 nm, and were always much less than the coherence lengths, as determined from the refractive index measurements.

The NLO properties of the films were subsequently investigated using second-harmonic generation. A Q-switched Nd:YAG laser ($\lambda = 1064$ nm) with a pulse width of 8 ns and a pulse energy of 10 mJ was used as the source of the fundamental, and a reference sample of Y-cut quartz ($d_{11} = 0.46$ pm/V) was used for calibration of the frequency-doubled signal.

Alignment of the NLO side groups in the films was achieved by single-point corona poling, with the point source held at $+10$ kV, at a distance of 1.5 cm from the surface. Increasing poling voltage led to an increase in

the harmonic intensity, i.e. maximum alignment was not achieved at this voltage. However, higher voltages occasionally resulted in damage to the sample surface. Hence, for comparison purposes, the voltage was limited to 10 kV. Because of the low glass transition temperatures of these polymers, the poling was carried out at room temperature, concurrent with the second-harmonic generation measurements. This arrangement had the advantage of reproducibility of the measurement condition for each layer. Following removal of the poling field, the second-harmonic signal decayed to zero within a few minutes.

The values of the second-harmonic coefficient, d_{33} , for samples 5-9 are listed in Table II. The values of d_{33} were obtained using the analysis of Jerphagnon and Kurtz (25), and were calculated under the assumption that the degree of alignment of the nonlinear optical chromophores can be described using the isotropic model. Hence, we assumed $d_{33}=3d_{31}$ (4).

Table II near here.

In the series of polymers 5-8, which contain the nitrostilbene side groups 1-3, the trend in the d_{33} value versus loading of the chromophoric side group was well reproduced, with d_{33} values in the range 4.1-5.0 pm/V. Note that the decrease in the spacer length from three to one ethyleneoxy units appeared to have no effect on the d_{33} value. For polymer 9, which contained the high β azo chromophore 4, the d_{33} value was 34 pm/V, which was significantly higher than for the stilbene substituted polymers that contained equivalent side group incorporation ratios. This is partially a consequence of the greater resonant enhancement, given the longer wavelength of the azo chromophore absorption peak.

Conclusions and Future Prospects

The synthetic versatility offered by the phosphazene system has allowed the preparation of polymers that contain nonlinear optical units as pendant side chains. Our future research on nonlinear optical polyphosphazenes will focus on tailoring the macromolecular system to generate higher glass transition temperatures. This, and the stabilized alignment of the chromophoric side groups, should be attainable by the incorporation of a third co-substituent that contains a crosslinkable moiety. Thus, crosslinking of the polymer matrix during the application of an electric field would be expected to stabilize the nonlinear optical character.

Acknowledgements

The work at The Pennsylvania State University was supported by the U.S. Office of Naval Research and the U.S. Air Force Office of Scientific Research. The work at the University of Southern California was supported by the U.S. Air Force of Scientific Research.

Literature Cited

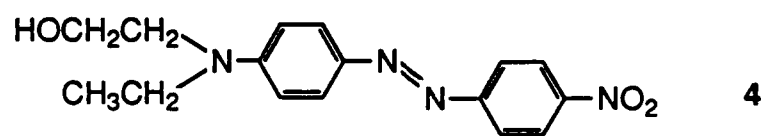
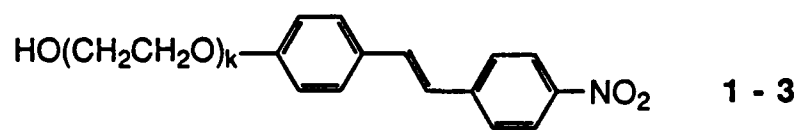
1. Chemla, D. S.; Zyss, J., Eds. Nonlinear Optical Properties of Organic Molecules and Crystals, Academic: New York, 1987; Vols. 1,2.
2. Khanarian, G., Ed. Molecular and Polymeric Optoelectronic Materials: Fundamentals and Applications: SPIE: Dan Diego, 1986; Vol. 682.
3. Williams, D. J., Ed. Nonlinear Optical Properties of Organic and Polymeric Materials; ACS Symposium Series 233; American Chemical

Society: Washington, DC, 1983.

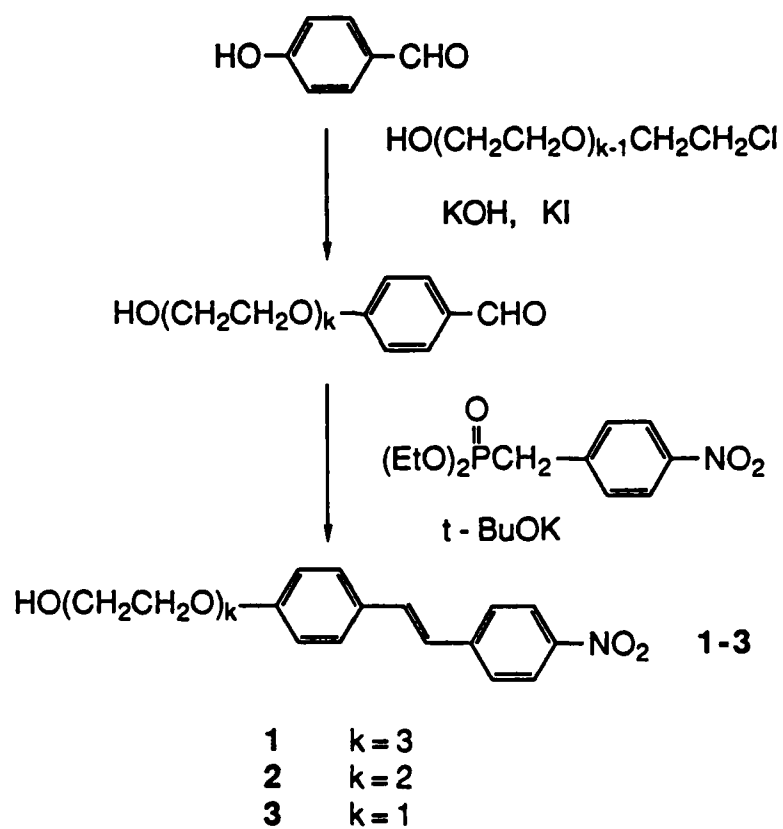
4. Williams, D. J. Agnew. Chem., Int. Ed. Engl. 1984, 23, 690.
5. Singer, K. D.; Sohn, J. E.; Lalama, S. J. Appl. Phys. Lett. 1986, 49, 248.
6. Hill, J. R.; Dunn, P. L.; Davies, G. J.; Oliver, S. N.; Pantelis, P.; Rush, J. D. Electronics Lett. 1987, 23, 700.
7. Hampsch, H. L.; Yang, J.; Wong, G. K.; Torkelson, J. M. Macromolecules 1988, 21, 526.
8. Meredith, G. R.; VanDusen, J. G.; Williams, D. J. Macromolecules 1982, 15, 1385.
9. Ye, C.; Marks, T. J.; Yang, J.; Wong, G. W. Macromolecules 1987, 20, 2322.
10. Leslie, T. M.; DeMartino, R. N.; Choe, E.; Khanarian, G.; Haas, D.; Nelson, G.; Stamatoff, J. B.; Stuetz, D. E.; Teng, C.; Yoon, H. Mol. Cryst. Liq. Cryst. 1987, 153, 451.
11. Singer, K. D.; Kuzyk, M. G.; Holland, W. R.; Sohn, J. E.; Lalama, S. J.; Comizzoli, R. B.; Katz, H. E.; Schilling, M. L. Appl. Phys. Lett. 1988, 53, 1800.
12. Eich, M.; Sen, A.; Looser, H.; Bjorklund, G. C.; Swalen, J. D.; Tweig, R.; Yoon, D. Y. J. Appl. Phys. 1989, 66(6), 2559.
13. Hall, H. J., Jr.; Kuo, T.; Leslie, T. M. Macromolecules 1989, 22, 3525.
14. Rubello, D. R. J. Polym. Sci.; Polym. Chem. 1990, 28, 1.
15. Dembek, A. A.; Kim, C.; Allcock, H. R.; Devine, R. L. S.; Steier, W. H.; Spangler, C. W. Chemistry of Materials, in press.
16. Allcock, H. R.; Kugel, R. L. J. Am. Chem. Soc. 1965, 87, 4216.
17. Allcock, H. R.; Kugel, R. L.; Valen, K. J. Inorg. Chem. 1966, 5, 1709.

18. Allcock, H. R.; Kugel, R. L. Inorg. Chem. 1966, 5, 1716.
19. Allcock, H. R. Chem. Eng. News 1985, 63, 22.
20. Allcock, H. R.; Allen, R. W.; Meister, J. J. Macromolecules 1976, 9, 950.
21. Allen, R. W.; Allcock, H. R. Macromolecules 1976, 9, 956.
22. Wadsworth, W.; Emmons, W. J. J. Am. Chem. Soc. 1961, 83, 1733.
23. Allcock, H. R.; Kim, C. Macromolecules 1989, 22, 2596.
24. Ferrar, W. T.; Marshall, A. S.; Whitefield, J. Macromolecules 1987, 20, 317.
25. Jerphangnon, J.; Kurtz, S. K. J. Appl. Phys. 1970, 41, 1667.

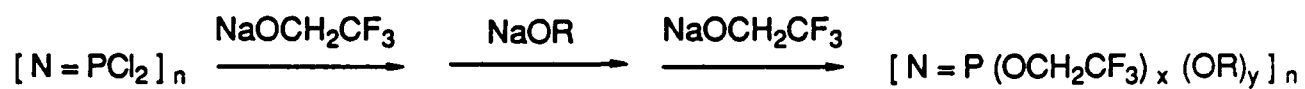
Figure 1



Scheme I



Scheme II



5 - 9

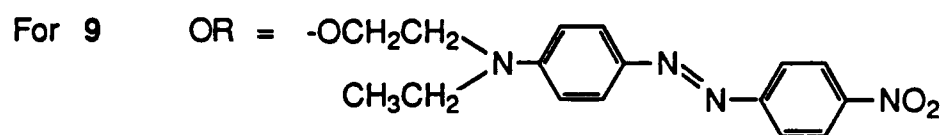
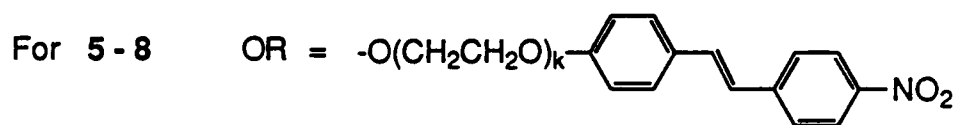


Table I
Polyphosphazene Structures and Composition Ratios

| Compd ^a | Side Group Structure ^b | y ^c , % |
|--------------------|-----------------------------------|--------------------|
| 5 | k = 3 | 26 |
| 6 | k = 3 | 36 |
| 7 | k = 2 | 39 |
| 8 | k = 1 | 31 |
| 9 | - | 33 |

^aSee Scheme II for general polymer structure

^bSee Figure 1 for general side group structure

^cx + y = 100%

Table II
 d_{33} Coefficients for Polyphosphazenes

| Compd ^a | d_{33} , pm/V |
|--------------------|-----------------|
| 5 (y=26%) | 4.1 |
| 8 (y=31%) | 4.7 |
| 6 (y=36%) | 5.0 |
| 7 (y=39%) | 5.0 |
| 9 (y=33%) | 34 |

^aSee Scheme II and Table I for polymer structures and composition ratios;
Polymers 5-8 arranged in order of increasing value of y

TECHNICAL REPORT DISTRIBUTION LIST, GENERAL

| | <u>No.</u> <u>Copies</u> | | <u>No.</u> <u>Copies</u> |
|--|------------------------------------|--|-----------------------------|
| Office of Naval Research Chemistry Division, Code 1113 800 North Quincy Street Arlington, VA 22217-5000 | 3 | Dr. Ronald L. Atkins Chemistry Division (Code 385) Naval Weapons Center China Lake, CA 93555-6001 | 1 |
| Commanding Officer Naval Weapons Support Center Attn: Dr. Bernard E. Doua Crane, IN 47522-5050 | 1 | Chief of Naval Research Special Assistant for Marine Corps Matters Code OOMC 800 North Quincy Street Arlington, VA 22217-5000 | 1 |
| Dr. Richard W. Drisko Naval Civil Engineering Laboratory Code L52 Port Hueneme, California 93043 | 1 | Dr. Bernadette Eichinger Naval Ship Systems Engineering Station Code 053 Philadelphia Naval Base Philadelphia, PA 19112 | 1 |
| Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314 | 2 <u>high</u> <u>quality</u> | Dr. Sachio Yamamoto Naval Ocean Systems Center Code 52 San Diego, CA 92152-5000 | 1 |
| David Taylor Research Center Dr. Eugene C. Fischer Annapolis, MD 21402-5067 | 1 | David Taylor Research Center Dr. Harold H. Singerman Annapolis, MD 21402-5067 ATTN: Code 283 | 1 |
| Dr. James S. Murday Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000 | 1 | | |

Dr. J. M. Augl
Naval Surface Weapons Center
White Oak, MD 20910

Dr. A. S. Abhiraman
School of Chemical Engineering
Georgia Institute of Technology
Atlanta, GA 30332

4132033

Dr. Harry R. Allcock
Department of Chemistry
Pennsylvania State University
University Park, PA 16802

Dr. Chris W. Allen
Department of Chemistry
University of Vermont
Burlington, VT 05405

4132007

413c012

Dr. Ronald D. Archer
Department of Chemistry
University of Massachusetts
Amherst, MA 01003

Dr. Ali S. Argon
Mechanical Engineering Department
Massachusetts Institute of Technology
Cambridge, MA 02139

413c028

a400005df

Dr. William J. Bailey
Department of Chemistry
University of Maryland
College Park, MD 20742

Dr. Kurt Baum
Fluorochem, Inc.
680 S. Ayon Avenue
Azusa, CA 91702

413a006

4000021sbi

Dr. Frank D. Blum
Department of Chemistry
University of Missouri - Rolla
Rolla, MO 65401

Dr. Len J. Buckley
Naval Air Development Center
Code 6063
Warminster, PA 18974

413m005

Dr. F. James Boerio
Materials Science & Engineering Dept.
University of Cincinnati
Cincinnati, Ohio 45221

Dr. Ivan Caplan
DTNSRDC Annapolis
Code 0125
Annapolis, MD 21401

413m012

Dr. Robert E. Cohen
Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139

4132001

Dr. E. Fischer
DTNSRDC Code 2853
Annapolis, MD 21402

Dr. Curtis W. Frank
Department of Chemical Engineering
Stanford University
Stanford, CA 94305

413h005

Dr. Gregory S. Girolami
School of Chemical Sciences
University of Illinois
Urbana-Champaign, IL 61801

4132014

Dr. Robert H. Grubbs
Department of Chemistry
California Institute of Technology
Pasadena, CA 91124

4132019

Dr. James F. Haw
Department of Chemistry
Texas A&M University
College Station, TX 77843

413c039

Dr. Stuart L. Cooper
Department of Chemical Engineering
University of Wisconsin
Madison, WI 53706

4132006

Dr. Warren T. Ford
Department of Chemistry
Oklahoma State University
Stillwater, OK 74078

413h006

Dr. John K. Gillham
Department of Chemical Engineering
Princeton University
Princeton, New Jersey 08544

413c005

Dr. Bernard Gordon
Department of Polymer Science
Pennsylvania State University
University Park, PA 16802

413c025

Dr. Henry K. Hall
Department of Chemistry
University of Arizona
Tucson, AZ 85721

413j009

Dr. Alan J. Heeger
Department of Physics
University of California, Santa Barbara
Santa Barbara, CA 93106

4132012

Dr. Pat J. Hendra
Department of Chemistry
University of Southampton
Highfield Southampton 509 5NH
United Kingdom
4134001

Dr. Bruce S. Hudson
Department of Chemistry
University of Oregon
Eugene, Oregon 97403

413c018

Dr. Hatsuo Ishida
Department of Macromolecular Science
Case Western Reserve University
Cleveland, OH 44106

413m008

Dr. Paul M. Lahti
Department of Chemistry
University of Massachusetts
Amherst, MA 01003

413c037

Dr. Robert W. Lenz
Polymer Science and Engineering Dept.
University of Massachusetts
Amherst, MA 01002

441c013

Dr. Alan D. MacDiarmid
Department of Chemistry
University of Pennsylvania
Philadelphia, PA 19104

a400004df

Dr. Charles E. Hoyle
Department of Polymer Science
University of Southern Mississippi
Hattiesburg, MS 39406-0076

413c026

Dr. Leonard V. Interrante
Department of Chemistry
Rensselaer Polytechnic Institute
Troy, NY 12181

413c014

Dr. Jeffrey T. Koberstein
Institute of Materials Science
University of Connecticut
Storrs, CT 06268

4132013

Dr. Richard M. Laine
Washington Technology Center
University of Washington
Seattle, WA 98195

s400033srh

Dr. Geoffrey Lindsay
Chemistry Division - Code 087
Naval Weapons Center
China Lake, CA 93555

4132036

Dr. Chris W. Macosko
Materials Science & Engineering Dept.
University of Minnesota
Minneapolis, MN 55455

4132029

Dr. Joseph H. Magill
Materials Science & Engineering Dept.
University of Pittsburgh
Pittsburgh, PA 15161

413c013

Dr. Tobin J. Marks
Department of Chemistry
Northwestern University
Evanston, IL 60201

413c030

Dr. Krzysztof Matyjaszewski
Department of Chemistry
Carnegie Mellon University
Pittsburgh, PA 15213

413j002

Dr. William B. Moniz
Code 6120
Naval Research Laboratory
Washington, DC 20375-5000

4132012

Dr. Virgil Percec
Department of Macromolecular Science
Case Western Reserve University
Cleveland, OH 44106-2699

413c024

Dr. Roger S. Porter
Dept. of Polymer Science & Engineering
University of Massachusetts
Amherst, MA 01002

413m006

Dr. Leo Mandelkern
Department of Chemistry
Florida State University
Tallahassee, FL 32306-3015

4132018

Dr. Lon J. Mathias
Department of Polymer Science
University of Southern Mississippi
Hattiesburg, MS 39406-0076

413m003

Dr. James E. McGrath
Department of Chemistry
Virginia Polytechnic Institute
Blacksburg, VA 24061

4132007

Dr. Kay L. Paciorek
Ultrasystems Defense and Space, Inc.
16775 Von Karman Avenue
Irvine, CA 92714

s400029srh

Dr. Martin Pomerantz
Department of Chemistry
University of Texas at Arlington
Box 19065
Arlington, TX 76019-0065
a400008df

Dr. T. J. Reinhart, Jr.
Nonmetallic Materials Division
Air Force Materials Laboratory (AFSC)
Wright-Patterson AFB, OH 45433

Dr. Arnost Reiser
Insitute of Imaging Sciences
Polytechnic University
333 Jay Street
Brooklyn, NY 11021

4132022

Dr. Charles M. Roland
Code 6120
Naval Research Laboratory
Washington, DC 20375-5000

413m009

Dr. Ronald Salovey
Department of Chemical Engineering
University of Southern California
Los Angeles, CA 90089

413m010

Dr. Jerry I. Scheinbeim
Dept. of Mechanics & Materials Science
Rutgers University
Piscataway, NJ 08854

4132009

Dr. L. E. Slotter
Code Air 931-A
Naval Air Systems Command
Washington, D. C. 20361-9310

Dr. Dietmar Seyferth
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139

413c004

Dr. Ferdinand Rodriguez
Department of Chemical Engineering
Cornell University
Ithaca, NY 14853

413c011

Dr. Michael F. Rubner
Materials Science & Engineering Dept.
Massachusetts Institute of Technology
Cambridge, MA 02139

413m007

Dr. Jacob Schaefer
Department of Chemistry
Washington University
St. Louis, MO 63130

413m001

Dr. Lawrence R. Sita
Department of Chemistry
Carnegie Mellon University
Pittsburgh, PA 15213

4132030

Dr. Richard R. Schrock
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139

4132038

Dr. David S. Soane
Department of Chemical Engineering
University of California, Berkeley
Berkeley, CA 94720-9989

413h004

Dr. Les H. Sperling
Materials Research Center #32
Lehigh University
Bethlehem, PA 18015

413c002

Dr. Richard S. Stein
Polymer Research Institute
University of Massachusetts
Amherst, MA 01002

4132008

Dr. C. S. Sung
Institute of Materials Science
University of Connecticut
Storrs, CT 06268

413m011

Dr. Sukant K. Tripathy
Department of Chemistry
University of Lowell
Lowell, MA 01854

4132016

Dr. C. H. Wang
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

413c020

Dr. Kenneth B. Wagener
Department of Chemistry
University of Florida
Gainesville, FL 32611

a400007df

Dr. Robert A. Weiss
Department of Chemical Engineering
University of Connecticut
Storrs, CT 06268

a400006df

Dr. George M. Whitesides
Department of Chemistry
Harvard University
Cambridge, MA 02138

4132010

Dr. Garth L. Wilkes
Department of Chemical Engineering
Virginia Polytechnic Institute
Blacksburg, VA 24061

4132020